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Development of a mechanistic model for mass transfer in sorption selective mixed-matrix membranes for gas separation

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Motivation

A promising new concept for membrane material is mixed-matrix membranes (MMM) consisting of a continuous polymeric phase and dispersed particles. These hybrid materials combine the advantages of polymeric and inorganic membrane materials. The crucial point for successful design of MMM is to match transport properties in both phases and therefore enhance permeability and selectivity in comparison to the pure polymer.[1)] In the last decade development of MMM for gas permeation has become a popular research area. In many publications glassy polymers are combined with zeolites or CMS to utilize the molecular sieving effect of these materials and separate gas molecules by size.[2)] With these combinations good results have been reached and the concept of MMM has been proven. But there are applications where molecular sieving is not the predominant separation effect, for example hydrocarbon dew point adjustment and solvent recovery. These applications require sorption selective membranes, because condensable components are separated from supercritical gases. For the design of a sorption selective mixed-matrix membrane a rubbery polymer can be used, because rubbery polymers are state of the art for solubility selective membranes. But it is not completely understood, which properties the inorganic filler needs to have in order to match the polymer.

This work is part of a project, in which sorption selective mixed-matrix membranes are developed for separation of n-butane and methane using PDMS, POMS and activated carbon. A mechanistic model is developed taking into account mass transport within and between both phases to be of avail choosing suitable carbon properties.

The new model

So far mass transport in mixed-matrix membranes is modelled with the Maxwell model and its enhancements, where total permeability is a function of permeability in both single phases (P_c and P_d) and phase fraction (□).[2)] Unfortunately, it is not possible to measure permeability through activated carbon, because it is in powder form. Therefore, in this work a mechanistic model for mass transport in a mixed-matrix membrane of PDMS and activated carbon is developed.

The model is based on a classical model for two-phase systems with axial mass transport, such as bubble columns or packed beds. It assumes that there is a mass transport normal to membrane surface in both phases and a mass transfer between them. Two phase regions alternate with layers of pure polymer, so that continuous phase encloses the dispersed phase completely, see figure 1.

In both phases diffusive mass transport is considered. Diffusion in polymer phase is assumed as continuum diffusion with a diffusion coefficient taken from literature. Diffusion within carbon is divided into pore and surface diffusion. The coefficients are calculated with suitable models after Knudsen (1950) and Okazaki (1981), taking into account thermodynamic and morphological parameters of the carbon, such as heat of adsorption and pore size distribution beside others.[3)] Mass transfer between polymer and inorganic phase is considered as diffusive mass transfer at a sphere. The resulting model equations account for sorption behaviour of polymer and carbon,

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diffusion coefficients, particle size and phase fraction. Also membrane thickness, feed and permeate pressure are integrated.

With this mechanistic model it is possible to calculate concentration profiles and mass transport within the membrane and analyse the influence of all different parameters.

Results

In figure 2 an example for plausibility of the model is given. The model was used to calculate the influence of dispersed phase fraction on total permeability of n-butane through a 20 µm thick membrane with p_{feed} = 1 bar and p_{perm} = 0,1 bar.

The layers of pure polymer between the two phase layers of polymer and carbon are of the same thickness as the two phase layers. Therefore the maximal phase fraction of particles in this structure is □ = 0.37, instead of □ = 0.74 (close sphere packing). Figure 2 shows that total permeability increases with increasing phase fraction. For low phase fractions up to □= 0.2 the new model agrees very well with the Maxwell model at a P_c/P_d ratio of 0.71. Calculating the ratio between mean mass flow through carbon and mean mass flow through polymer in all two-phase layers of the membrane, that is the ratio of permeabilities according to the new model, the same value is reached:

$$\frac{\bar{N}_{diff,poly}}{\bar{N}_{diff,carbon}} = \frac{P_c}{P_d}\bigg|_{Maxwell} = 0.71$$

The new model is therefore in very good agreement with the Maxwell model for low phase fractions. In parallel work D. Hülagü (TU Berlin) and H. Mushardt (Helmholtz-Zentrum-Geesthacht) are currently performing experimental investigations of the MMM, that will deliver data for validation.

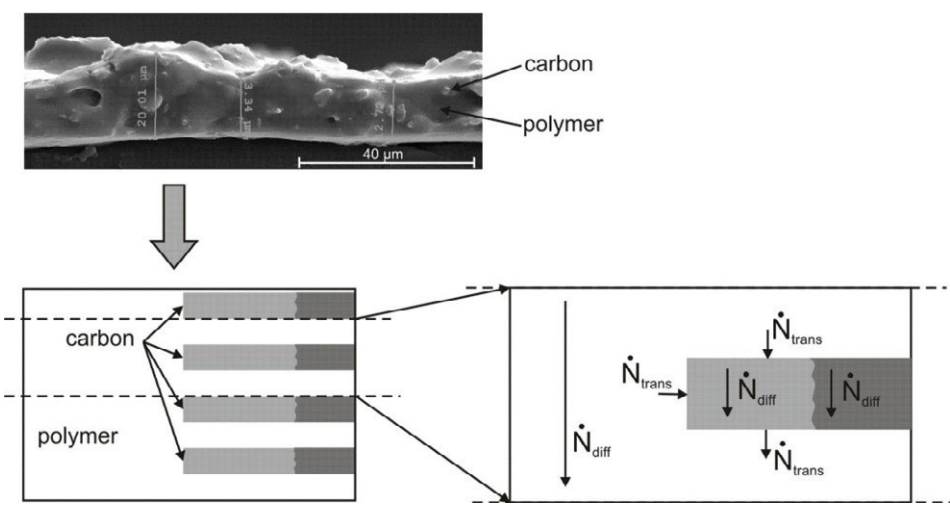

Figure 1: SEM picture of a PDMS-carbon MMM, simplified model configuration and considered mass flows

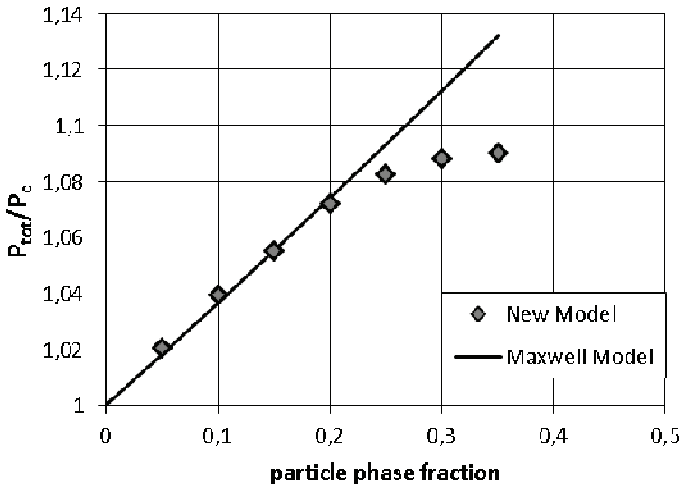

Figure 2: Comparison of the new model and the Maxwell model for n-butane permeability as a function of phase fraction

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